

LOWER WATER ABSORPTION DENTAL RESTORATIVE

This application is a continuation-in-part of my copending application, Ser. No. 873,600 filed Nov. 3, 1969, now abandoned, which was a continuation-in-part of my copending applications Ser. No. 713,318 filed Mar. 15, 1968 and Ser. No. 744,326, filed July 12, 1968, now U.S. Pat. Nos. 3,597,389 and 3,541,068, respectively.

This invention relates to improved moldable dental restorative compositions comprising acrylate or methacrylate esters of hydroxyalkyl ethers, i.e., hemiethers with di- or tri-primary diols or triols, of diphenols. In these restorative compositions, polymerization is initiated by free-radical generating catalysts. After polymerization is initiated the material is placed in cavities in teeth to provide polymeric restorations having excellent resistance to moisture, good strength and durability under oral conditions.

The filling or restoration of a cavity in a tooth is necessary to protect the tooth from further decay and eventual deterioration to the point at which it becomes a liability either because it introduces a source of infection or because it is so painful as to be intolerable. For many years, various types of fillings have been employed such as metals, either silver amalgams, gold or even other metals, and also various inorganic cement compositions such as silicates.

The difficulties with most of these fillings have been well recognized. Metallic fillings do not usually provide good sealing around the margins and infections can penetrate and develop in back of them. Furthermore, they give a somewhat unsightly contrast to the whiteness of teeth.

Silicate cements have been widely used but, in general, are relatively sensitive to leaching and deterioration under the moist conditions of the mouth.

Polymeric materials have been used for restorations by polymerization of various compositions in situ. Some such compositions included polymerized material suspended, or even partially dissolved, in monomer giving a polymeric restoration. Other restoratives are of the nature of polymerizable materials or binders with suspended inorganic fillers. This invention relates particularly to cavity-filling restoratives of this last category.

There are at least four criteria which can be applied to the restorative material and pertain especially to the binder.

1. Low toxicity.
2. Necessity for relatively low viscosity to permit use in filled dental restorative compositions.
3. Stability in oral conditions.
4. Compressive strength, particularly after exposure to oral conditions.

Toxicity is not so much the toxicity of ingestion, although unpleasant vapors and odor are objectionable, so much as it is the irritant effect of penetrating dental tubules and inflaming the pulp. This is particularly likely to be encountered when using binders comprising lower esters, such as methyl methacrylate, which have unpleasant odors and are relatively quite irritant. Previously proposed restorative compositions which included a suspension of polymethyl methacrylate in the monomer were obviously disadvantageous in this respect.

In order for the dentist to be able to force the restorative into the cavity rapidly before it hardens, it must be a composition having the proper consistency which is somewhat like putty. Of course, it must also be possible to include particulate filler which strengthens the ultimate restoration. Because the level of particulate filling is preferably relatively high, of the order of 60-80%, mixing of the binder with particulate filler is most readily effected without occluding much air if the viscosity of the binder is relatively low, below 10,000 centipoises. Binders with higher viscosities can be diluted with a lower ester such as methyl methacrylate and, in fact, that is found to be necessary in practice when using many prior art binders.

Stability in the oral cavity and retention of a reasonable level of strength are found to be largely a function of the absence of hydrophilic groups which enhance moisture absorption by the polymer. Binders, such as those of Bowen, U.S. Pat. No. 3,066,112, made by condensation of glycidyl methacrylate with phenols, e.g., bisphenol A, of necessity include hydroxyl groups from opening of an epoxy or oxirane ring and therefore are significantly hydrophilic. Furthermore, these materials have relatively high viscosities, of the order of 25,000 to 50,000 centipoises and higher, even to 250,000 and; as noted by Bowen, in order to be of use in dental binders must normally be diluted using a reactive diluent such as methyl methacrylate or tetraethylene glycol dimethacrylate. The former is, of course, one of the materials noted above as possessing toxicity.

Compressive strength of polymeric restoratives even containing silane treated inorganic fillers, has been relatively low as compared to amalgam fillings or the strength of the tooth structure itself. This is a distinct disadvantage from the standpoint of permanence of fillings as lowered compressive strength results in more rapid attrition.

In previous application, Ser. No. 713,318, now U.S. Pat. No. 3,597,389, it was pointed out that polycarbinol polymethacrylates and polyacrylates are valuable binders for dental purposes. It has been found that the polycarbinols which are hemiethers of certain diphenols form polymethacrylates which are resistant to hydrolytic degradation and have excellent properties for dental purposes as they have good strength and low sensitivity to moisture and when combined with suitable inorganic fillers, provide restorations matching the general tooth color for anterior and posterior teeth with relatively limited shrinkage on polymerization and favorable characteristics of thermal expansion over a range covering any normal oral conditions from about 0° to about 60° C.

It is an aim of this invention to provide polycarbinol polymethacrylates for dental applications. Other aims and objects will become evident from reading this application.

It has been found that especially valuable monomers for the compounding of restorative compositions are the polymethacrylates of diol and triol hemiethers of diphenols, which are free from active hydrogen atoms and may be formed by the esterification of primary hydroxyl terminated hydroxyalkylethers of diphenols. It should be noted that "polymethacrylate" in this usage does not refer to a polymer but to the presence of two or three methacrylate residues in a monomer. Those skilled in the art will recognize that the basic diphenolic compound is etherified at each phenolic OH by one OH